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(54) Title: WATERBORNE POLYMER COMPOSITION HAVING A SMALL PARTICLE SIZE (57) Abstract <p>The present invention is directed to a waterborne polymer composition having an average particle size of less than 70 nm which is prepared as an emulsion containing one or more monoethylenically unsaturated monomer, a sulfopolyester, water, and an initiator. The waterborne polymer composition is useful in size compositions for slasher dyeing of textiles to provide fibrous articles with excellent yarn abrasion resistance, blocking, water resistance, wet fastness/bleeding, and dry and wet crock resistance. In addition, the waterborne polymer composition is useful in formulations for cleaning and protecting hard surfaces.</p>		

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WATERBORNE POLYMER COMPOSITION HAVING A SMALL PARTICLE SIZE

Field of the Invention

This invention is directed to a waterborne polymer composition having a average particle size of less than 70 nm which is useful in size compositions for slasher dyeing of
5 textiles and in formulations for cleaning and protecting hard surfaces.

Background of the Invention

In the production of textile materials, it is generally
10 necessary to apply a coating or size to the fibers to improve or increase their stiffness, strength, smoothness or weight in order to protect the fibers from abrasion during the weaving process. The size must be flexible and tough since the fibers, threads or filaments are twisted and bent in various directions and rub
15 against the loom parts.

A large number of synthetic fiber sizing agents, which are either water-soluble or dilute alkali-soluble, have been employed to size the fibers with variable success. Such fiber sizing agents include polyacrylic acid, partially hydrolyzed polymers of
20 acrylonitrile and/or lower alkyl acrylate, maleic anhydride copolymers, maleic acid half-ester copolymers, polyvinyl alcohol, etc. However, some of these materials are not readily compatible with or do not adhere well to textile yarns and thus do not form a sufficient protective coating or film thereon. Other materials
25 cover the yarn but do not impart more than a slight degree of abrasion resistance. Still other materials, while coating the yarn in a satisfactory manner, are easily removed from the woven fabric and therefore are not suitable for slasher dyeing of textiles.

In the case of slasher dyeing applications, commercially
30 available synthetic fiber sizing agents have been blended with a crosslinker and a catalyst for pigment binding and adhesion to the fiber. The most common crosslinker is melamine formaldehyde which generates formaldehyde during curing or drying. Due to
35 strict regulations issued by Occupational Safety and Health

Agency (OSHA) and Environmental Protection Agency (EPA) to reduce or eliminate formaldehyde and other volatile organic compounds (VOCs), it is desirable to eliminate the crosslinker requirement. Thus, a need exists for sizing compositions which avoid the above-mentioned disadvantages.

U.S. Pat. No. 3,546,008 discloses non-crystalline polyesters which contain a hydrophobic moiety and a hydrophilic moiety. The sizing preparation comprises linear, water-dissipatable polyesters derived from a dicarboxylic acid, a diol wherein at least 20 mole percent of said diol component is polyethylene glycol, and a difunctional dicarboxylic acid sulfomonomer.

U.S. Patent No. 4,268,645 discloses a sizing composition containing a polyester resin having (1) a backbone portion comprising the reaction product of dihydroxy compound having a maximum molecular weight of 250 and dicarboxylic acid compound wherein the acid number of said backbone portion is less than 3 and (2) internal and pendant carboxylic acid moieties comprising an aromatic polycarboxylic acid compound having at least 3 acyl moieties.

U.S. Patent No. 5,156,651 discloses a graft polyester containing a metal sulfonate group for use in sizing textile threads and fibers. The sulfonated polyester carries grafts derived from a monomeric composition based on (a) at least one carboxylic acid unsaturated through ethylene, (b) butylacrylate or a mixture of monomers containing from 60-70% by weight of butyl acrylate, and (c) at least one carboxylic acid ester, unsaturated through monoethylene.

Other water-dispersible and water-dissipatable polyesters containing metal salt groups are known which are used as adhesives, coating materials including sizing materials, films and other products. Such polyesters are described in U.S. Pat. No. 3,779,993, U.S. Pat. No. 4,156,073 and U.S. Pat. No. 3,385,811. U.S. Pat. No. 4,156,073 also teaches polyfunctional acids such as trimellitic anhydride and pyromellitic acid as useful in the preparation of the linear polyesters.

Formulations for cleaning and protecting hard surfaces usually contain acrylic polymers, detergent-type surfactants, tripropylene glycol or a short chain alkyl ether of tripropylene

glycol as a hydrophobic solvent, and other minor ingredients. Such formulations can be used to clean hard surfaces, but do not improve the shine of the hard surfaces. In addition, there are formulations which improve the shine of hard surfaces, but do not
5 clean the hard surface.

U.S. Patent No. 4,869,934 discloses an aqueous cleaning, coating and polishing composition containing an acrylic polymer, a styrene-acrylic copolymer, a plasticizer, an anionic or a nonionic fluorocarbon surfactant, a preservative, and ammonia to
10 provide a pH of 8.0 to 9.6. While the composition disclosed in U.S. Patent No. 4,869,934 cleans and may protect surfaces, it does not provide a gloss or shine to the surfaces.

Summary of the Invention

Accordingly, it is an object of the present invention to
15 provide a waterborne polymer that is useful in size compositions for slasher dyeing of textiles.

Accordingly, it is another object of the present invention is to provide a waterborne polymer that is useful in formulations for cleaning and protecting hard surfaces.

20 With regard to the foregoing, the present invention is directed to a waterborne polymer composition having a average particle size of less than about 70 nm and a solids content of about 10 to about 45 weight percent. The waterborne polymer composition is useful in size compositions for slasher dyeing of
25 textiles to provide fibrous articles with excellent yarn abrasion resistance, blocking, water resistance, wet fastness/bleeding, and dry and wet crock resistance. In addition, the waterborne polymer composition is useful in formulations for cleaning and protecting hard surfaces to provide shine or gloss to the
30 surfaces. The waterborne polymer composition is prepared from an emulsion, said emulsion comprising:

- (A) about 10 to about 50 weight percent of one or more monoethylenically unsaturated monomer;
- (B) about 1 to about 10 weight percent of a water
35 dispersible sulfopolyester produced by the reaction of:
 - (a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids,

saturated aliphatic dicarboxylic acids,
cycloaliphatic dicarboxylic acids, and
combinations thereof;

(b) a diol; and

(c) a difunctional sulfomonomer containing at least
one sulfonate group attached to an aromatic
nucleus wherein the functional groups are hydroxy,
carboxy or amino, provided the difunctional
sulfomonomer is present in an amount from 12 to 25
mole percent based on 100 mole percent
dicarboxylic acid and 100 mole percent diol; and

(C) about 40 to about 90 weight percent water,
wherein the weight percents are based on the total weight of the
emulsion, and the emulsion has an average particle size of less
than about 70 nm and a solids content of about 10 to about 45
weight percent and is substantially free of formaldehyde
generating components.

According to another aspect of the present invention, a
process is provided for preparing a waterborne polymer
composition comprising the steps of:

I. preparing an emulsion containing water, about 10 to about 50
weight percent of one or more monoethylenically unsaturated
monomers, and about 1 to about 10 weight percent of a water
dispersible sulfopolyester; and

II. heating the emulsion prepared in Step I in the presence of
0.1 to 1 weight percent of an initiator which is effective
to start the polymerization of the monoethylenically
unsaturated monomers, to a temperature of 40°C to 90° C to
form a waterborne polymer composition,

wherein the weight percents are based on the total weight of the
waterborne polymer composition, and the waterborne polymer
composition has an average particle size of less than about 70 nm
and a solids content of about 10 to about 45 weight percent and
is substantially free of formaldehyde generating components.

Description of the Invention

The present invention is directed to a waterborne polymer
composition having an average particle size of less than about 70

nm which is prepared as an emulsion containing one or more monoethylenically unsaturated monomer, a sulfopolyester, water, and an initiator.

Component (A) of the waterborne polymer composition is one or more monoethylenically unsaturated monomer. Suitable monoethylenically unsaturated monomers include styrene, α -methyl styrene, methacrylate (MA), methylmethacrylate (MMA), ethyl acrylate (EA), butylacrylate (BA), butylmethacrylate (BMA), 2-ethylhexylacrylate (EHA), 2-hydroxyethyl acrylate (HEA), hydroxyethylmethacrylate (HEMA), acrylic acid (AA), acrylamide, maleic anhydride, acrylonitrile, and their derivatives. Preferably, the waterborne polymer is prepared using a combination of monoethylenically unsaturated monomers. The preferred monoethylenically unsaturated monomers are styrene, acrylic acid, methylmethacrylate, butylacrylate, butylmethacrylate, and hydroxyethylmethacrylate.

In the case where more than one monoethylenically unsaturated monomer is used, the monoethylenically unsaturated monomers having a glass transition temperature (T_g) of greater than 90°C such as styrene and methylmethacrylate should be present within about 10 percent of the monoethylenically unsaturated monomers having a T_g of less than 90°C. The monoethylenically unsaturated monomer is added in an amount of 10 to 50 weight percent, preferably 20 to 35 weight percent, based on the total weight of the waterborne polymer composition.

Component (B) of the waterborne polymer composition is a water-dispersible or water-dissipatable linear sulfopolyester. The sulfopolyester contains repeat units from a dicarboxylic acid, a diol and a difunctional sulfomonomer. The sulfomonomer must be present in an amount of at least 12 mole percent of the dicarboxylic acid component based on 100 mole percent dicarboxylic acid and 100 mole percent diol.

The dicarboxylic acid component of the sulfopolyester includes aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, saturated aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, and cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of suitable dicarboxylic acids are: terephthalic acid, phthalic

acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like. The sulfopolyester may be prepared from two or more of the above dicarboxylic acids.

It should be understood that use of the corresponding acid anhydrides, esters, and acid chlorides of these acids is included in the term "dicarboxylic acid".

The diol component of the sulfopolyester includes cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of suitable diols are: ethylene glycol, diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, and 2,2-bis-(4-hydroxypropoxyphenyl)-propane. The sulfopolyester may be prepared from two or more of the above diols.

The difunctional sulfomonomer component of the sulfopolyester is a dicarboxylic acid or an ester thereof containing a sulfonate group ($--SO_3^-$). The cation of the sulfonate salt may be Na^+ , Li^+ , K^+ , NH_4^+ , and substituted ammonium. The term "substituted ammonium" refers to ammonium substituted with an alkyl or hydroxy alkyl radical having 1 to 4 carbon atoms. Examples of suitable difunctional sulfomonomers are: sulfophthalic acid, sulfoterephthalic acid, sulfoisophthalic acid, 4-sulfonaphthalene-2,7-dicarboxylic acid, and their esters. The difunctional sulfomonomer must present in an amount of at least 12 mole percent, preferably 15 to 25 mole percent, and most preferably 17 to 20 mole percent, based on 100 mole percent dicarboxylic acid.

The inherent viscosity of the sulfopolyester is 0.1 to 0.5 dl/g as measured in a 60/40 parts by weight solution of

phenol/tetrachloroethane at 25°C. at a concentration of 0.25 grams of sulfopolyester in 100 mL of the solvent. Preferably, the inherent viscosity of the sulfopolyester is 0.28 to 0.35 dl/g. The sulfopolyester is added in an amount of 1 to 10 weight percent, preferably 4 to 6 weight percent, based on the total weight of the waterborne polymer composition.

Component (C) of the waterborne polymer composition is water. Tap water or distilled water may be used. Distilled water is preferred. Water is added in an amount of 40 to 90 weight percent, preferably 65 to 80 weight percent, based on the total weight of the waterborne polymer composition.

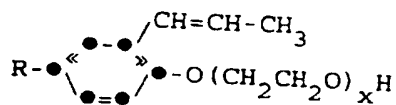
Component (D) of the waterborne polymer composition is an initiator. The initiator must be effective to start the polymerization of the monoethylenically unsaturated monomer and result in a polymer having an average particle size less than about 70 nm. It is important to note that the waterborne polymer composition having a average particle size of less than 70 nm cannot be prepared using the following conventional water-soluble initiators: ammonium persulfate, sodium persulfate, and potassium persulfate. Preferably, the initiator used to prepare the waterborne polymer composition is a combination of either t-butylhydrogen peroxide/ Fe^{2+} /isoascorbic acid or t-butylhydrogen peroxide/ Fe^{2+} /ascorbic acid. Such preferred initiators have been shown to produce stable emulsions having an average particle size of less than 70 nm. The initiator is added in an amount of 0.01 to 1 weight percent, preferably 0.05 to 0.25 weight percent, based on the total weight of the waterborne polymer composition.

The process for preparing the waterborne polymer compositions of the present invention involves polymerizing in the form of an emulsion the monoethylenically unsaturated monomers in the presence of an aqueous dispersion of a sulfopolyester, an initiator, and an optional surfactant. It is important to note that the sulfopolyester, component (B), acts as a stabilizer in the amount used herein, however, an optional surfactant may also be added.

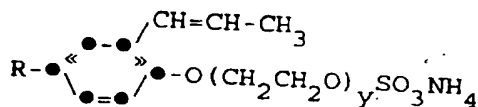
Suitable optional surfactants include any water soluble or dispersible surfactant with a hydrophilic-lipophilic balance

(HLB) value greater than 7.0. The amount of surfactant used in emulsifying ingredients of the present invention is in the range of 0.01 to 1.0, preferably 0.05 to 0.5 weight percent based on total weight of the acrylic polymer composition. Examples of surfactants are: ionic and nonionic surfactants such as alkyl polyglycol ethers such as ethoxylation products of lauryl, oleyl, and stearyl alcohols; alkyl phenol polyglycol ethers such as ethoxylation products of octyl- or nonylphenol, diisopropyl phenol, triisopropyl phenol; alkali metal ammonium salts of alkyl, aryl or alkylaryl sulfonates, sulfates, phosphates, and the like, including sodium lauryl sulfate, sodium octylphenol glycoether sulfate, sodium dodecylbenzene sulfonate, sodium lauryldiglycol sulfate, and ammonium tritertiarybutyl phenol and penta- and octa-glycol sulfonates, sulfosuccinate salts such as disodium ethoxylated nonylphenol half ester of sulfosuccinic acid, disodium n-octyldecyl sulfosuccinate, and sodium dioctyl sulfosuccinate.

The optional surfactant can also be reactive anionic or nonionic surfactants possessing styrene or allyl groups. Examples include surface active monomers sold by PPG Industries, Inc., under the trademark SAM 181, 183, 184, and 211 which are anionic sulfates or sulfonates and SAM 185-187 which are nonionic. Other reactive surfactants include those sold by Daiichi Kogyo Seiyaku under the trademark AQUARON. Examples of AQUARON surfactants includes compounds of the formulae



and



wherein R is a C₁-C₁₂ alkyl group and x and y are integers of from 1 to 5. Other reactive surfactants include the sodium alkyl allyl sulfosuccinate sold by Henkel, under the trademark TREMLF-40.

Preferably, the process for preparing the waterborne polymer composition of the present invention involves: (1) mixing one of the optional surfactants with an aqueous dispersion of water dispersible sulfopolyester; (2) preparing a mixture of the monoethylenically unsaturated monomers to form a monomer mixture which is added to the sulfopolyester dispersion slowly under constant agitation to prepare a oil-in-water emulsion; (3) heating a portion of the emulsion, preferably 20 to 40 weight percent based on the total emulsion, to a temperature of 40°C to 90° C in a reaction flask; (4) slowly adding the remaining portion of the emulsion and initiator separately by means of a pump to the emulsion in the reaction flask; (5) maintaining the temperature in the reaction flask at 40°C to 90° C for a sufficient time, preferably 30 to 60 minutes, to form a waterborne polymer composition; and (6) allowing the waterborne polymer composition to cool to room temperature before removing from the reaction flask and filtering. It is important to note that the present inventors have determined that a narrower range of particle size or more uniform particle size is achieved by heating a portion of the emulsion before combining with the remaining portion of emulsion.

Additives such as wetting agents, leveling agents, defoaming agents, solvents, fillers, lubricants, ultraviolet light absorbing agents, preservatives, antioxidants, buffers, colorants, dyes, and pigments normally used in sizing compositions or formulations for cleaning or protecting may be used if desired. Such additives, their amounts, and their use are well known.

The waterborne polymer compositions of this invention are useful in size compositions for slasher dyeing with and without pigment on such substrates as nylon, acetate, cotton, polyester, acrylic yarn and fabric. In addition, the waterborne polymer compositions are useful in formulations for cleaning and protecting hard surfaces. Suitable hard surfaces include tile, concrete, wood, formica, metal, glass and ceramic.

The materials used for the results shown herein are as follows:

Waterborne polymer Compositions:

<u>Ingredients</u>		<u>Waterborne polymer Compositions</u>				
		A	B	C	D	E
5	Polyester	5.00	3.00	5.0	5.00	5.0
	Styrene	30.00	30.00	50.0	50.00	50.0
	Acrylic Acid	1.50	1.50	1.5	1.50	1.5
	HEMA	2.50	2.50	2.5	2.50	0.0
	BA	25.00	25.00	41.0	41.00	43.5
10	MMA	20.00	20.00	0.0	0.00	0.0
	BMA	16.00	18.00	0.0	0.00	0.0
	HEA	0.00	0.00	0.0	0.00	0.0
	Surfactant	0.08	0.08	0.1	0.12	0.1

<u>Properties</u>		<u>Waterborne polymer Compositions</u>				
		A	B	C	D	E
15	Solids %	35.0	35.0	35.0	35.0	30.0
	pH	6.3	4.1	5.0	4.6	4.5
	T _g (°C)	27.8	27.2	10.4	10.4	6.7
	Particle Size (nm)	54.0	60.0	55.0	59.0	59.0

20 The testing procedures used for the results shown herein are as follows:

(1) Abrasion Tests

Yarn abrasion resistance of the sized material was studied by the following two methods:

- 25 (a) Duplan Test: A single end of yarn is warped around several hooks to form a web of 20 passes. A group of weighed blades are placed on the yarn web. The blades of the Duplan machine are oscillated back and forth in order to cause the yarn filaments to separate. The yarns are abraded until there are 10 failures out of 20, then the number of abrasion cycles is recorded.
- 30 (b) Zweigle Test: Twenty separate yarns are tied off across an abrasion cylinder covered with sand-paper. The tester is programmed for the desired test conditions and testing is started. The cylinder moves back and forth while turning in order to abrade the yarn samples. The tester stops after all the yarns
- 35

have broken. The program calculates the number of cycles at which each yarn broke and determines an average for the series of yarns.

(2) Blocking Test

5 The sized yarns are parallel wound in order to simulate a warp beam. The parallel spools (tubes) are placed in a humidity chamber to condition the yarn for a period of 7 days at 90% RH (relative humidity) and 95°F. After 7 days, the amount of
10 tension to remove the yarn is measured with a tensiometer to evaluate blocking. If the sized yarns stick together it means blocking.

(3) Wet/Dry Crocking Test

15 The crock-fastness is determined by using the standard AATCC test method: "Color-fastness to Crocking: AATCC Crock-Meter Method".

(4) Wet-Fastness To Bleed Test

20 A 2" x 4" sample of the treated fabric is placed in 110°F water for 30 minutes. The sample is removed after 30 minutes and the absorbance of the water is measured using a Spectrophotometer at 525 nm.

The following examples are intended to illustrate, but not limit, the scope of this invention. All parts and percentages in the examples are on a weight basis unless otherwise stated.

Example 1

The Waterborne polymer Compositions A-E and WD-30 were diluted to 8.0% solid with water and evaluated for adhesion, blocking and tackiness on MYLAR polyester film. WD-30 is a commercially available 30% dispersion of a sulfopolyester in water. The sulfopolyester in WD-30 has a glass transition temperature of 29°C and is prepared from isophthalic acid, 5-sodiosulfoisophthalic acid, and diethylene glycol. The test results are summarized in Table I.

TABLE I

Waterborne Acrylic Polymer	Blocking Resistance	Tackiness	Adhesion	
			Tape Test	Rapid Flex
A	No	No	40/40	40/40
B	No	No	40/40	40/40
C	No	No	40/40	40/40
D	No	No	40/40	40/40
E	No	No	40/40	40/40
WD-30	50%-80% Blocked	No	8/40	0/40

The test results in Table I indicate that the Waterborne polymer Compositions A-E displayed no blocking on MYLAR polyester film. In contrast, the WD-30 exhibited 50% to 80% blocking on the MYLAR polyester film. Waterborne polymer Compositions A-E showed excellent abrasion resistance on yarn as measured by Duplan Abrasion Test. In addition, the Waterborne polymer Compositions A-E have superior adhesion to the polyester yarn as compared to adhesion to MYLAR polyester film based on the tape test and rapid flex tests which were repeated 40 times and the Waterborne polymer Compositions A-E displayed 100% pass rate. The superior adhesion of Acrylic polymer compositions A-E to yarn may be due to the difference in flat versus curved surfaces, and also surface energy difference of the two surfaces.

Example 2

Waterborne polymer Compositions A-E and commercial product WD-30 were evaluated for water resistance at 80°C. The test results are summarized in Table II.

TABLE II

5	Acrylic Polymer Compositions	Water Resistance at 80°C (minutes)				
		1	2	3	5	10
	A	1	1	1	1	1
	B	1	1	1	1	1
	C	1	1	1	1	1
10	D	1	1	1	1	1
	E	1	1	1	1	1
	WD-30	2	3	4	5	

Rating Scale:

- 15 1 - No Change in Appearance; 2 - Slightly Cloudy; 3 - Cloudy and Starting to Soften; 4 - Very Soft and Partially Dissolved; 5 - Dissolved Completely

20 The test results in Table II clearly indicate that Acrylic Polymer Compositions A-E display no water absorbance even after 10 minutes. Moreover, Acrylic Polymer Compositions A-E are much more water resistant than the WD-30 which completely dissolved in water after only five minutes.

Example 3

25 In this example, the Waterborne polymer Compositions were evaluated under desizing conditions. Slasher dyeing is also known as permanent sizing, since the size composition should not be removed from the yarn and/or fabric.

30 Aqueous solutions containing 7.5% solids were prepared from the Waterborne polymer Compositions A-E. A pigment millbase was mixed with each of the aqueous dispersions of Waterborne polymer Compositions A-E such that the final concentration of pigment was 8.0 wt %. Each of the compositions was padded onto 100% polyester fabric. The dyed fabric was dried at 275°F for 30 seconds, and then dried at 325° for 15 seconds. The dyed fabric was tested for color fastness according to AATCC Crock-Meter

Method. Several tests were performed for desizing on the fabric. The test results are summarized in Table III.

TABLE III

5	Waterborne Acrylic Polymer Compositions	Desizing at 80°C	
		Water	Scour ¹
	A	**	**
	B	**	**
	C	**	**
10	D	**	**
	E	**	**
	WD-30	17 Seconds	24 Seconds

¹ - Noninoic Detergent 0.5 g/l + Sodium Carbonate 0.5 g/l.
 ** = No removal after 2 minutes in desizing bath.

15 The test results in Table III indicate that Waterborne polymer Compositions A-E are not removed from the fabric even after 2 minutes under desizing conditions. In contrast, WD-30 was removed from the fabric in only 17 seconds with water and in only 24 seconds with detergent.

20 Example 4

In this example, the Waterborne polymer Compositions A-E were evaluated against WD-30 sulfopolyester with a maleated melamine formaldehyde resin (CYMEL-373) which is a formaldehyde generating crosslinker in permanent slasher dyeing of textiles.
 25 Permanent slasher dyeing formulations were prepared as follows:

<u>Ingredients</u>	Amount	
	(g)	(%)
Waterborne polymer Compositions A-E (30.0% solid)	15.0	17.5

15

Blue Pigment-16	16.0	8.0
Water	169.0	84.5

Commercial Product		
WD-30 (30.0% solid)	7.2	3.6

5 CYMEL 373	1.0	0.5
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Ammonium Nitrate (10% solid)	20.0	10.0
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Blue Pigment - 16	16.0	8.0
Water	155.8	77.9

- 10 The permanent slasher dyeing formulations were used to dye a polyester fabric using the procedure described in Example 3. The fabric was evaluated for color transfer both in the wet and dry conditions. The test results are summarized in Table IV.

TABLE IV

5	Waterborne Acrylic Polymer <u>Composition</u>	Wet Fastness/ Bleed <u>Test</u>	Color Transfer (Crock) Test	
			<u>Dry Test</u>	<u>Wet Test</u>
	A	1	2-3	2-3
	B	1	2-3	2-3
	C	1	2-3	2-3
	D	1	2-3	2-3
10	E	1	-	-
	WD-30	3-4	3	4

Rating Scale: 1 - No Color Transfer; 2 - Slight Color Transfer; 3 - Significant Color Transfer; 4 - Complete Color Transfer

15 The test results in Table IV indicate that the permanent
slasher dyeing formulations containing the Waterborne polymer
Compositions A-E transferred less color in both wet and dry
conditions from the fabric as compared to the permanent slasher
dyeing formulations containing WD-30 sulfopolyester and
20 formaldehyde generating crosslinker.

Example 5

Example 4 was repeated except that WD-30 was mixed with
Waterborne polymer Compositions A-E in a ratio of 1.0% to 15.0
wt % to prepare permanent slasher dyeing formulations. The
25 results indicated that the addition of WD-30 sulfopolyester to
Waterborne polymer Compositions A-E did not change wet
fastness/bleed or dry and wet crock test data. Thus, color
transfer from the fabric was not affected by addition of WD-30
sulfopolyester to the Waterborne polymer Compositions of the
30 present invention.

Example 6

Example 4 was repeated except that cotton fabric was used instead of polyester fabric in the permanent slasher dyeing process. Permanent slasher dyeing formulations containing Waterborne polymer Compositions A-E showed only slight color transfer in wet and dry conditions from the cotton fabric.

Example 7

Example 4 was repeated except that the polyester fabric was used for permanent sizing of the back side of the polyester fabric. Permanent slasher dyeing formulations containing the Waterborne polymer Compositions A-E transferred less color in both wet and dry conditions from the fabric as compared to the permanent slasher dyeing formulations containing WD-30 sulfopolyester and formaldehyde generating crosslinker.

Example 8

This example illustrates the preparation and composition of a cleaner and protectant formulation containing Waterborne polymer Compositions A-E. The Waterborne polymer Compositions were diluted with water to obtain about 10 wt % solids. The diluted compositions were applied on Formica and vinyl tiles using spray device or pre-moistened wipe. The gloss of the coated surface was measured using a Gloss Meter (Labor-Reflektometer RL3 from DR Lange, Berlin, Germany). The test results are summarized as an average of three readings in Table V.

TABLE V

Waterborne Acrylic <u>Polymer Compositions</u>		<u>Gloss at 60°C</u>
5	A	45.2
	B	47.4
	C	52.5
	D	38.8
	E	48.3

10 The test results in Table V indicates that gloss varies in the range of 38 to 53 at 60°. The gloss of the coated Formica surface increased by about 1.5-2.0 times as compared to no coating.

Example 9

15 Example 8 was repeated except that about 8 to 10 weight percent of water was replaced with a solvent (ethylene glycol monobutyl ether) to prepare a cleaner and protectant formulation. Waterborne polymer Compositions A-E were diluted with water to contain about 10 weight percent solids. The diluted compositions were applied on Formica and vinyl tiles by means of a spray
20 device or pre-moistened wipes. The gloss of the cleaned surface was measured using a Gloss Meter (Labor-Reflektometer RL3 from DR Lange, Berlin, Germany). The test results are summarized as an average of three readings in Table VI.

TABLE VI

Waterborne Acrylic <u>Polymer Compositions</u>		<u>Gloss at 60°</u>
25	A	56.2
	B	52.4
	C	56.5
	D	48.8
	E	55.3

30 The test results in Table V indicates that gloss varies in the range of 48 to 57 at 60°. The gloss of the cleaned Formica surface was higher after cleaning the vinyl and Formica surfaces.

The present inventors have determined that a waterborne polymer composition having a average particle size of less than 70 nm will adhere to and bind together the several filaments of textile yarns and provide abrasion resistance to such yarns during weaving. Moreover, the acrylic polymer composition is not removable from textile yarns by scouring. In addition, the acrylic polymer composition cleans and provides a protective shine on hard surfaces. Moreover, the small particle size of the waterborne polymer compositions forms a smooth film.

Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious modifications are within the full intended scope of the appended claims.

WHAT IS CLAIMED IS:

1. An emulsion for making a waterborne polymer composition, said emulsion comprising:

- 5 (A) about 10 to about 50 weight percent of one or more monoethylenically unsaturated monomer;
- (B) about 1 to about 10 weight percent of a water dispersible sulfopolyester produced by the reaction of:
- 10 (a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof;
- (b) a diol; and
- 15 (c) a difunctional sulfomonomer containing at least one sulfonate group attached to an aromatic nucleus wherein the functional groups are hydroxy, carboxy or amino, provided the difunctional sulfomonomer is present in an amount from 12 to 25 mole percent based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and
- 20 (C) about 40 to about 90 weight percent water, wherein the weight percents are based on the total weight of the emulsion, and the emulsion has an average particle size of less than about 70 nm and a solids content of about 10 to about 45 weight percent and is substantially free of formaldehyde
- 25 generating components.

2. An emulsion for making a waterborne polymer composition, said emulsion comprising:

- 5 (A) 20 to 35 weight percent of one or more monoethylenically unsaturated monomer;
- (B) 4 to 6 weight percent of a water dispersible sulfopolyester produced by the reaction of:
- 10 (a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof;

- (b) a diol; and
- (c) a difunctional sulfomonomer containing at least one sulfonate group attached to an aromatic nucleus wherein the functional groups are hydroxy, carboxy or amino, provided the difunctional sulfomonomer is present in an amount from 12 to 25 mole percent based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and
- (C) 65 to 80 weight percent water, wherein the weight percents are based on the total weight of the emulsion, and the emulsion has an average particle size of less than about 70 nm and a solids content of about 10 to about 45 weight percent and is substantially free of formaldehyde generating components.

3. The emulsion of Claim 1 wherein the monoethylenically unsaturated monomer is selected from the group consisting of styrene, α -methyl styrene, methacrylate, methylmethacrylate, ethyl acrylate, butylacrylate, butylmethacrylate, 2-ethylhexylacrylate, 2-hydroxyethyl acrylate, hydroxyethylmethacrylate, acrylic acid, acrylamide, maleic anhydride, acrylonitrile, and combinations thereof.

4. The emulsion of Claim 3 wherein the monoethylenically unsaturated monomer is a combination of styrene, acrylic acid, methylmethacrylate, butylacrylate, butylmethacrylate, and hydroxyethylmethacrylate.

5. The emulsion of Claim 1 wherein 20 to 60 weight percent of the monoethylenically unsaturated monomer is styrene.

6. The emulsion of Claim 1 wherein the dicarboxylic acid component of the sulfopolyester is selected from the group consisting of terephthalic acid, phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, and combinations thereof.

7. The emulsion of Claim 6 wherein the dicarboxylic acid component of the sulfopolyester is isophthalic acid.

8. The emulsion of Claim 1 wherein the diol component of the sulfopolyester is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, and combinations thereof.

9. The emulsion of Claim 8 wherein the diol component is a mixture of diethylene glycol and 1,4-cyclohexanedimethanol.

10. The emulsion of Claim 1 wherein the difunctional sulfomonomer component of the sulfopolyester is selected from the group consisting of sulfophthalic acid, sulfoterephthalic acid, sulfoisophthalic acid, 4-sulfonaphthalene-2,7-dicarboxylic acid, and esters thereof.

11. The emulsion of Claim 10 wherein the difunctional sulfomonomer is 5-sodio-sulfoisophthalic acid.

12. An emulsion for making a waterborne polymer composition, said emulsion comprising:

(A) about 10 to about 50 weight percent of one or more monoethylenically unsaturated monomer;

(B) about 1 to about 10 weight percent of a water dispersible sulfopolyester produced by the reaction of:

(a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof;

(b) a diol; and

(c) a difunctional sulfomonomer containing at least one sulfonate group attached to an aromatic nucleus wherein the functional groups are hydroxy, carboxy or amino, provided the difunctional sulfomonomer is present in an amount from 12 to 25

mole percent based on 100 mole percent
dicarboxylic acid and 100 mole percent diol;
20 (C) about 40 to about 90 weight percent water; and
(D) about 0.1 to about 1 weight percent of an initiator
which is effective to start the polymerization of the
monoethylenically unsaturated monomers,
wherein the emulsion has an average particle size of less than
25 about 70 nm and a solids content of about 10 to about 45 weight
percent and is substantially free of formaldehyde generating
components.

13. The emulsion of Claim 12 wherein the initiator is selected
from the group consisting of t-butylhydrogen peroxide/ Fe^{2+} /isoascorbic acid and t-butylhydrogen peroxide/ Fe^{2+} /ascorbic
acid.

14. The emulsion of Claim 1 which additionally contains 0.01 to
1 weight percent of a surfactant selected from the group
consisting of ionic and nonionic surfactants.

15. The emulsion of Claim 1 which additionally contains an
additive selected from the group consisting of wetting agents,
leveling agents, defoaming agents, solvents, fillers, lubricants,
ultraviolet light absorbing agents, preservatives, antioxidants,
5 buffers, colorants, dyes, pigments, and combinations thereof.

16. A waterborne polymer composition which comprises:
(A) about 70 to about 98 weight percent of a polymer;
(B) about 0.4 to 5 weight percent of a water dispersible
sulfopolyester produced by the reaction of:
5 (a) a dicarboxylic acid selected from the group
consisting of aromatic dicarboxylic acids,
saturated aliphatic dicarboxylic acids,
cycloaliphatic dicarboxylic acids, and
combinations thereof;
10 (b) a diol; and
(c) a difunctional sulfomonomer containing at least
one sulfonate group attached to an aromatic

15 nucleus wherein the functional groups are hydroxy,
carboxy or amino, provided the difunctional
sulfomonomer is present in an amount from 12 to 25
mole percent based on 100 mole percent
dicarboxylic acid and 100 mole percent diol; and
(C) water,

20 wherein the weight percents are based on a total solids content
of about 10 to about 45 weight percent of the the waterborne
polymer composition, and the waterborne polymer composition has
an average particle size of less than about 70 nm and is
substantially free of formaldehyde generating components.

17. A process for preparing a waterborne polymer composition
comprising the steps of:

- 5 I. preparing an emulsion containing water, about 10 to about 50
weight percent of one or more monoethylenically unsaturated
monomers, and about 1 to about 10 weight percent of a water
dispersible sulfopolyester produced by the reaction of:
- 10 (a) a dicarboxylic acid selected from the group consisting
of aromatic dicarboxylic acids, saturated aliphatic
dicarboxylic acids, cycloaliphatic dicarboxylic acids,
and combinations thereof;
- (b) a diol; and
- 15 (c) a difunctional sulfomonomer containing at least one
sulfonate group attached to an aromatic nucleus wherein
the functional groups are hydroxy, carboxy or amino,
provided the difunctional sulfomonomer is present in an
amount from 12 to 25 mole percent based on 100 mole
percent dicarboxylic acid and 100 mole percent diol;
and
- 20 II. heating the emulsion prepared in Step I in the presence of
0.1 to 1 weight percent of an initiator which is effective
to start the polymerization of the monoethylenically
unsaturated monomers, to a temperature of 40°C to 90° C to
form a waterborne polymer composition,
- 25 wherein the weight percents are based on the total weight of the
waterborne polymer composition, and the waterborne polymer
composition has an average particle size of less than about 70 nm

and a solids content of about 10 to about 45 weight percent and is substantially free of formaldehyde generating components.

18. A process for preparing a waterborne polymer composition comprising the steps of:

I. preparing an emulsion containing water, about 10 to about 50 weight percent of one or more monoethylenically unsaturated monomers, and about 1 to about 10 weight percent of a water dispersible sulfopolyester produced by the reaction of:

(a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof;

(b) a diol; and

(c) a difunctional sulfomonomer containing at least one sulfonate group attached to an aromatic nucleus wherein the functional groups are hydroxy, carboxy or amino, provided the difunctional sulfomonomer is present in an amount from 12 to 25 mole percent based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and

II. heating the emulsion formed in Step I in the presence of 0.1 to 1 weight percent of an initiator which is selected from the group consisting of t-butylhydrogen peroxide/ Fe^{+2} /isoascorbic acid and t-butylhydrogen peroxide/ Fe^{+2} /ascorbic acid, to a temperature of 40°C to 90° C to form a waterborne polymer composition,

wherein the weight percents are based on the total weight of the waterborne polymer composition, and the waterborne polymer composition has an average particle size of less than about 70 nm and a solids content of about 10 to about 45 weight percent and is substantially free of formaldehyde generating components.

19. The waterborne polymer composition prepared by the process of Claim 16.

20. A fibrous article sized with the composition of Claim 1.

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21. A hard surface having applied thereon the composition of Claim 1.

INTERNATIONAL SEARCH REPORT

Int. Appl. No.
PCT/US 97/11569

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F283/02 C09D167/02 C09D151/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F C08L C09D D06M D06P C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 4 939 233 A (JENKINS WAYLON L ET AL) 3 July 1990 see column 3, line 14 - column 6, line 12 see column 2, line 45 - column 3, line 13 ---	1-4,6-19 20,21
Y	GB 1 551 126 A (BASF AG) 22 August 1979 see page 3, line 73-85 ---	20,21
X	US 4 946 932 A (JENKINS WAYLON L) 7 August 1990 see the abstract see column 3, line 1 - column 7, line 54 ---	1-19 20,21
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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